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黄射干的异黄酮类成分

许云龙 马云保 熊 江
(中国科学院昆明植物研究所植物化学开放实验室, 昆明 650204)

摘要 从黄射干 *Iris tectorrum* 的甲醇抽提物中分到5个异黄酮: 鸢尾黄酮甲素 (1), 鸢尾花素 (2), 野鸢尾黄酮 (3), 鸢尾黄酮 (4), 鸢尾黄酮甙 (5)。化合物 (1) 和 (2) 系首次从黄射干中分到。所有成分经详细光谱分析确定。

关键词 黄射干, 鸢尾科, 异黄酮, 鸢尾黄酮甲素, 鸢尾花素, 野鸢尾黄酮, 鸢尾黄酮, 鸢尾黄酮甙。
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Isoflavonoids of *Iris tectorrum*

XU Yun-Long MA Yun-Bao XIONG Jiang
(*Laboratory of Phytochemistry*, *Kunming Institute of Botany*, *The Chinese Academy of Sciences*, Kunming 650204)

Abstract Five isoflavanoids had been isolated from the methanolic extract of *Iris tectorrum* . They were iristectorigenin A (1), irisflorentin (2), irigenin (3), tectorigenin (4) and tectoridin (5). Compound (1) and (2) were isolated from this plant for the first time. All of the compounds were identified on the basis of detailed spectroscopic analysis including two-dimensional NMR (^{1}H-^{1}H COSY; ^{1}H-^{13}C COSY) data.
Key words *Iris tectorrum* , Iridaceae, Isoflavanoids, Iristectorigenin A, Irisflorentin, Irigenin, Tectorigenin, Tectoridin.

INTRODUCTION

The crude drug Huang-She-Gan (*Iris tectorrum*) is used in Chinese traditional medicine for influenza, breathing canal infection, and throat swelling (Jiangsu New Medical College, 1977). The rhizomes of *Iris tectorrum* was used as She-Gan (*Belamcanda chinensis*) in Yunnan and South China. Five isoflavanoids together with β-sitosterol and daucosterol had been isolated from the methanolic extract of this plant. Those compounds were characterized as iristectorigenin A (1), irisflorentin (2), irigenin (3), tectorigenin (4) and tectoridin (5). Compound (1) and (2) were isolated from *Iris tectorrum* for the first time.

The present paper describes the isolation, structural elucidation and identification of isoflavanoids from *Iris tectorrum* .

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RESULTS AND DISCUSSION

The spectral data indicated that compounds 1 ~ 5 have a similar constitution. Furthermore, these compoents are analogous to tectorigenin 4' - glucoside (6) isolated from *Iris crocea* (Shawl *et al*, 1992), and dichotomitin (7) isolated from *Iris dichotoma* (Li *et al*, 1986) and analogous to noririsflorentin (8) and belamcanidin (9) isolated from *Belamcanda chinensis* (Woo *et al*, 1993; Yamaki *et al*, 1990). 1 ~ 5 are all isoflavonoids.

Iristectorigenin A (1), $C_{17}H_{14}O_7$, M^+ 330, have strong IR absorption bands for hydroxyl groups (3450, 3420 cm^{-1}). There were characteristic peaks due to the isoflavonol skeleton (1655, 1617, 1575, 1515, 980, 955 cm^{-1}). This was further supported by typical UV maxima at 215.5, 268 nm (Shawl *et al*, 1992). The ^{13}C NMR data (Table 2) also revealed the signals of a carbon skeleton of an isoflavone and two methoxyl groups. The locations attached of two methoxyl and three hydroxyl groups were deduced as follows. Mass spectrometry also supported the presence of a hydroxyl group and a methoxyl group in ring B by giving retro - Diels - Alder giving the ions at m/z 148 and 139 (Kachroo *et al*, 1990; Agarwal *et al*, 1984). The extreme downfield characteristic signal at δ13.80 ppm could be assigned to 5 - OH due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). In addition, the downfield signal at δ3.97 ppm could be assigned to 6 - OMe due to the deshielding effect of two ortho - hydroxyl groups (Li *et al*, 1986). The ^{13}C NMR data of ring B revealed the presence of 3' - OH, 4' - OMe moiety (Markham *et al*, 1978).

Irisflorentin (2), $C_{20}H_{18}O_8$, M^+ 386, differs from noririsflorentin (8) by the presence of an MeO signal at δ4.09 in 2, which replaced the 5 - OH signal at ~ δ13.7 ppm in (8) (Woo *et al*, 1993). On the basis of the above evidence and the ^{13}C NMR data, we assigned 2 as irisflorentin, namely 6, 7 - methylenedioxy - 3', 4', 5', 5 - tetramethoxyisoflavone.

Irigenin (3), $C_{18}H_{16}O_8$, M^+ 360; Mass spectrometry revealed the presence of a hydroxyl group and two methoxyl group in ring B by retro - Diels - Alder giving the ions at m/z 153 and 183 (Kachroo *et al*, 1990; Agarwal *et al*, 1984). The ^{13}C NMR data of ring B also supported the presence of 3' - OH, 4' - OMe, 5' - OMe moiety (Markham *et al*, 1978). Therefore, on the basis of the above evidence, we could assign 3 as irigenin, namely 3', 5, 7 - trihydroxy - 4', 5', 6 - trimethoxyisoflavone.

Tectorigenin (4), $C_{16}H_{12}O_6$, M^+ 300; Mass spectrometry revealed the presence of a hydroxyl group in ring B by retro - Diels - Alder giving the typical ions at m/z 118 and 182 (Kachroo *et al*, 1990; Agarwal *et al*, 1984). The ^{13}C NMR data of ring B also supported the presence of 4' - OH moiety (Markham *et al*, 1978). So, 4 could be assigned as tectorigenin, namely 4', 5, 7 - trihydroxy - 6 - methoxyisoflavone. This conclusion was further confirmed by the detailed $^1H - ^1H$ COSY and $^1H - ^{13}C$ COSY data (Table 4) (Morita *et al*, 1972a).

Tectoridin (5), $C_{22}H_{22}O_{11}$, M^+ 462; differs from 4 by the presence of extra glucose signals. The extreme downfield characteristic (13.54 ppm signal could be assigned to 5 - OH due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). The ^{13}C NMR data of ring B are same with

that of 4. Thus, 5 could assign as tectoridin, namely 4', 5 – dihydroxy – 7 – (β – D – glucopyranosyloxy) – 6 – methoxyisoflavone.

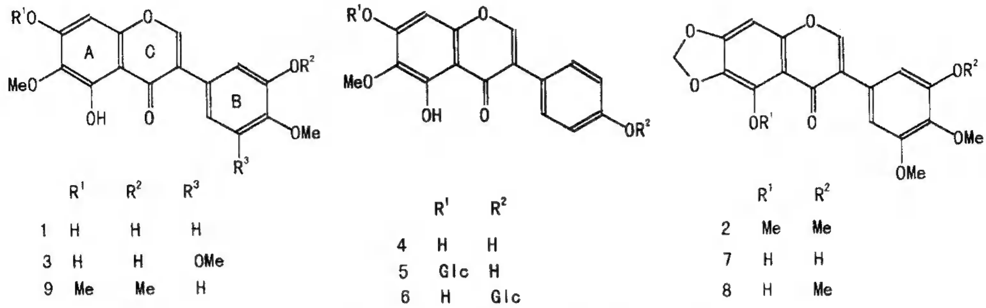

Fig. 1 Soflavanoids of *Iris tectorum* and analogus

EXPERIMENT

General. Kofler melting points were uncorrected; Optical ratations were taken on a Jasco – 20C digital polarimeter. IR were recorded on KBr discs with a Perkin – Elmer 577 spectrometer. UV were obtained in EtOH on a UV – 210A spectrometer. EIMS (positive) were measured on a VG Auto Spec – 3000 spectrometer with direct inlet 70 or 20 eV. NMR were run on a Bruker AM – 400 specrtometer using TMS as internal. standard; chemical shift values are reported in δ (ppm) units (pyridine – d_5 and $CDCl_3$). Coupling constants (J) were expressed in Hz.

Plant Material. The rhizomes of *Iris tectorrum* was purchased in Kunming Company of Medical Materia, Yunnan, China. in Sept, 1993 and identified by Prof. Jingsheng Yang. A voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica.

Extraction and isolation. Dried and powdered roots (5.0 kg) were repeatedly soaked with cool MeOH for 5 days x 5 and then concd. to give the crude residue (662.5 g). The residue (661.5 g) was suspended in 2 l. H_2O and the suspension extracted with petroum ether (750 mL × 2), EtOAc (750 mL × 3), and n – BuOH (500 mL × 3) saturated with H_2O respectively. The petroum ether soln was evapd in vacuum to obtained 30 g yellow syrup. The EtOAc soln was evapd in vacuum to yield 141.5 g yellow gum. The n – BuOH soln were also evapd in vacuum to contain 75 g brown gums. The EtOAc fraction was mixed with silica gel (137.5 g, 200 ~ 300 mesh) and subjected to CC over silica gel (1494 g, 200 ~ 300 mesh) eluting with $CHCl_3$ by increasing amounts of MeOH to obtain 2 (500 mg, 0.01%), β – sitosterol (100 mg, 0.002%), 3 (100 mg, 0.002%), 1 (70 mg, 0.0014%), 4 (2.0 g, 0.04%), daucosterol (500 mg, 0.01%). 5 (2.0 g, 0.04%). Some components were further purified by recrystallization and prep. TLC (silica gel).

Iristectorigenin A (1), $C_{17}H_{14}O_7$; mp. 232 ~ 235℃; UVλ_{max}^{MeOH} 215.5, 268 nm; IRν_{max}^{KBr} cm^{-1}: 3450, 3420, 1655, 1617, 1575, 1515, 1458, 1415, 1375, 1325, 1300, 1278, 1262, 1245, 1210, 1190, 1152, 1120, 1068, 1028, 980, 955, 885, 860, 813, 783, 755, 734, 720, 675, 563; EIMS (70eV) m/z (%): 330 $[M]^+$ (100), 315 $[M-CH_3]^+$ (40), 312 $[M-H_2O]^+$ (38), 287 $[M-CO-CH_3]^+$ (50), 272 $[M-CO-2\times CH_3]^+$ (6), 257 [M – CO – CH_3 – OMe

+1]$^+$ (1), 149 [CH=C-B-ring +1]$^+$ (21), 148 [CH=C-B-ring]$^+$ (10), 139 [A-ring+1]$^+$ (15), 135 (10), 117 (12), 105 (18), 93 (5), 77 (18), 69 (42), 40 (25); ^{1}H NMR (C_5D_5N) δ: see Table 1. ^{13}C NMR data (C_5D_5N) δ: see Table 2.

Irisflorentin (2), $C_{20}H_{18}O_8$; mp. 164 ~ 165℃; UVλ_{max}^{MeOH} 205.5, 220, 264, 322 nm; IRν_{max}^{KBr} cm^{-1}: 1662, 1625, 1600, 1580, 1505, 1478, 1432, 1415, 1360, 1340, 1310, 1275, 1130, 1105, 1055, 1030, 1000, 930, 852, 845, 810, 755, 660; EIMS (70eV) m/z (%): 386 [M]$^+$ (100), 371 [M-CH_3]$^+$ (12), 358 [M-CO]$^+$ (25), 343 [M-CO-CH_3]$^+$ (92), 325 [M-OCH_3-OCH_2]$^+$ (15), 315 [M-OCH_2O-CH_3]$^+$ (10), 297 [315-H_2O]$^+$ (8), 285 (12), 194 [M-CH=C-B-ring]$^+$ (6), 193 [CH=C-B-ring+1]$^+$ (5), 192 [CH=C-B-ring]$^+$ (2), 177 (80), 149 [A-ring-1]$^+$ (67), 134 [A-ring -CH_3-1]$^+$ (50), 119 [A-ring -OCH_3]$^+$ (44), 106 (25), 77 (54), 63 (72), 53 (49), 40 (31); ^{1}H NMR ($CDCl_3$) δ: see Table 1. ^{13}C NMR data ($CDCl_3$) δ: see Table 2.

Table 1 ^{1}H NMR Chemical Shifts of Compounds 1, 3, 4, 5 in C_5D_5N, 2 in $CDCl_3$.

Hydrogen	1	2	3	4	5
H-2	8.21 s	7.81 s	8.22 s	8.15 s	8.13 s
H-8	6.77 s	6.65 s	6.71 s	6.75 s	7.19 s
5-OH	13.80 br s		13.70 br s	13.77 br s	13.54 br s
H-2'	7.50 d, 1.6	6.76 s	7.32 d, 1.6	7.74 d, 9.1	7.70 d, 8.4
H-3'				7.3 d, 9.1	
H-4'					
H-5'	7.12 d, 9.0			7.31 d, 9.1	7.28 d, 8.4
H-6'	7.32 dd 9.0, 1.6	6.76 s	6.97 d, 1.6	7.74 d, 9.1	7.70 d, 8.4
OCH_2O		6.08 s			
G-1-H					5.82 d, 6.8
G-H_6					4.63-4.24 m
5-OCH_3		4.09 s			
6-OCH_3	3.97 s		3.91 s	3.98 s	4.05 s
3'-OCH_3		3.89 s			
4'-OCH_3	3.85 s	3.87 s	3.87 s		
5'-OCH_3		3.89 s	3.82 s		

Irigenin (3), $C_{18}H_{16}O_8$; mp. 168 ~ 171℃; UVλ_{max}^{MeOH} 217.5, 267, 322.5 nm; IRν_{max}^{KBr}cm^{-1}: 3450, 3420, 1660, 1628, 1615, 1575, 1505, 1458, 1440, 1425, 1375, 1350, 1330, 1300, 1260, 1210, 1198, 1160, 1115, 1075, 1060, 980, 965, 898, 845, 815, 810, 770, 710, 594, 540; EIMS (70eV) m/z (%): 360 [M]$^+$ (100), 345 [M-CH_3]$^+$ (27), 330 [M-2xCH_3]$^+$ (20), 317 [M+ -CO-CH_3]$^+$ (45), 299 [317-H_2O]$^+$ (5), 287 [M-CO-3xCH_3]+ (9), 183 [M-CH=C-B-ring+1]$^+$ (5), 163 (6), 153 [B-ring]$^+$, 150 (10), 121 [A-ring-OH]$^+$ (15), 105 (8), 93 (8), 77 (16), 69 (39), 63 (19), 53 (15), 40 (10); ^{1}H NMR (C_5D_5N)δ: see Table 1. ^{13}C NMR data (C_5D_5N)δ: see Table 2.

Tectorigenin (4), $C_{16}H_{12}O_6$; mp. 214 ~ 216℃; UVλ_{max}^{MeOH} 213, 266, 321 nm; IRν_{max}^{KBr}cm^{-1}: 3600, 3450, 3315, 1650, 1618, 1605, 1582, 1570, 1508, 1453, 1440, 1362, 1328, 1290,

1246, 1218, 1180, 1160, 1114, 1060, 987, 833, 812, 755, 675, 590; EIMS (70eV) m/z (%): 300 $[M]^+$ (77), 285 $[M-CH_3]^+$ (29), 282 $[M-H_2O]^+$ (30), 271 $[M-CO-1]^+$ (3), 257 $[M-CO-CH_3]^+$ (100), 182 $[M-CH=C-B-ring]^+$ (2), 150 $[M-CH=C-B-ring-OCH_3-1]^+$ (10), 139 $[A-ring+1]^+$ (26), 119 $[CH=C-B-ring+1]^+$ (20), 118 $[CH=C-B-ring]^+$ (9), 101 (10), 93 $[B-ring]^+$ (6), 89 (12), 77 (17), 69 (70), 63 (15), 43 (10), 40 (20); ^{1}H NMR (C_5D_5N)δ: see Table 1. ^{13}C NMR data (C_5D_5N)δ: see Table 2.1

Table 2 ^{13}C NMR Chemical Shifts of Compounds 1, 3, 4, 5 in C_5D_5N, 2 in $CDCl_3$.

Carbon	1	2	3	4	5
2	153.82 d	150.71 d	154.32 d	153.66 d	154.03 d
3	122.83 s	125.68 s	123.24 s	123.31 s	123.45 s
4	181.68 s	175.17 s	181.44 s	181.73 s	181.74 s
5	159.11 s	154.65 s	159.17 s	159.36 s	157.70 s
6	132.75 s	135.61 s	132.79 s	132.78 s	133.84 s
7	154.68 s	141.75 s	154.68 s	154.71 s	154.51 s
8	94.98 d	93.22 d	95.03 d	95.03 d	94.91
9	154.03 s	152.91 s	154.07 s	154.10 s	153.38 s
10	106.22 s	113.80 s	106.18 s	106.27 s	107.79 s
1'	122.83 s	127.38 s	127.59 s	122.53 s	122.17 s
2'	114.05 d	106.81 d	111.70 d	131.19 d	131.07 d
3'	148.60 s	153.12 s	152.27 s	116.47 d	116.43 d
4'	148.71 s	138.23 s	138.00 s	159.14 s	159.40 s
5'	116.65 d	153.12 s	153.95 s	116.47 d	116.43 d
6'	122.69 d	106.81 d	105.45 d	131.19 d	131.07 d
Glucose					
1					102.11 d
2					74.75 d
3					78.67 d
4					71.29 d
5					79.47 d
6					62.56 t
OCH_2O		102.20 t			
5-OCH_3		61.25 q			
6-OCH_3	60.40 q		60.52 q	60.47 q	60.87 q
3'-OCH_3		56.28 q			
4'-OCH_3	56.14 q	60.82 q	60.37 q		
5'-OCH_3		56.28 q	56.19 q		

Tectoridin (5), $C_{22}H_{22}O_{11}$; mp. 258 ~ 260; UVλ_{max}^{MeOH} 208.5, 267, 331 nm ; IRν_{max}^{KBr} cm^{-1}: 3460, 3400, 3360, 1652, 1615, 1605, 1575, 1515, 1455, 1410, 1360, 1315, 1290, 1273, 1249, 1228, 1116, 1090, 1080, 1040, 1015, 994, 978, 925, 810, 780, 760, 745, 706, 600; HRMS m/z: 462.1167, Calc. for $C_{22}H_{22}O_{11}$ 462.1162; EIMS (70eV) m/z (%): 300 $[M-Glc]^+$ (100), 285 $[300-CH_3]^+$ (42), 282 $[300-H_2O]^+$ (48), 271 $[300-CO-1]^+$ (6), 257 $[300-CO-CH_3]^+$ (78), 226 $[257-OCH_3]^+$ (2), 182 $[M+-Glc-CH=C-B-ring]^+$ (1), 153 $[O-A-ring-Glc-1]^+$ (11), 139 $[A-ring-Glc+1]^+$ (24), 119 [CH = C - B -

ring + 1]$^+$ (18), 118 [CH = C - B - ring]$^+$ (18), 97 (14), 93 [B - ring]$^+$ (10), 89 (17), 77 (21), 73 (28), 69 (79), 57 (33), 43 (70); ^{1}H NMR (C_5D_5N) (: 13.54 (1H, s, 5 - OH), 8.13 (1H, s, 2 - H), 7.70 (2H, d, 8.4 Hz, 2', 6' - H), 7.28 (2H, d, 8.4 Hz, 3', 5' - H), 7.19 (1H, s, 8 - H), 5.82 (1H, d, 6.8, G - 1 - H), 4.63 (1H, dd, 12.0, 1.6, G - 6 - Ha), 4.42 (1H, dd, 9.6, 6.8, G - 2 - H), 4.41 (1H, dd, 12.0, 5.2, G - 6 - Hb), 4.40 (1H, t, 9.6, G - 3 - H), 4.32 (1H, t, 9.6, G - 4 - H), 4.24 (1H, ddd, 9.6, 5.2, 1.6, G - 5 - H), 4.05 (3H, s, 6 - OMe). ^{13}C NMR data (C_5D_5N) δ: see Table 2.

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